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MLM--2906 (OP)

HYDROGEN DIFFUSION AND ELECTRONIC STRUCTURE

DE82 008460

IN CRYSTALLINE AND AMORPHOUS $Ti_y CuH_x$

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ABSTRACT

Hydrogen diffusion behavior and electronic properties of crystalline $TiCuH_{0.94}$, $Ti_2CuH_{1.90}$, and $Ti_2CuH_{2.63}$ and amorphous $a-TiCuH_{1.4}$ are studied using proton relaxation times, proton Knight shifts, and magnetic susceptibilities. Crystal structure and hydrogen site occupancy have major roles in hydrogen mobility. The density of electron states at E_F is reduced in amorphous $a-TiCuH_{1.4}$ compared to the crystalline hydrides.

The crystalline intermetallics TiCu and Ti_2Cu and the amorphous $Ti_{1-y}Cu_y$ $(0.3 \leq y \leq 0.7)$ alloys directly react with gaseous hydrogen to form crystalline and amorphous ternary hydrides,[1-4] respectively, providing the temperature is maintained below 200°C. A recent nuclear magnetic resonance (NMR) study of the proton relaxation times[5] indicated a much higher hydrogen mobility in amorphous $a-TiCuH_{1.3}$ compared

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to polycrystalline $TiCuH_{0.94}$. The increased disorder[3] of interstitial hydrogen occupancy in a-TiCuH$_x$ has been suggested[5] for the enhanced mobility in the amorphous phase. The present paper describes further NMR studies of diffusion in crystalline and amorphous TiCuH$_x$ as well as crystalline Ti$_2$CuH$_x$. Furthermore, the electronic structure has been investigated using magnetic susceptibility, proton spin-lattice relaxation time (T$_1$), and proton Knight shift (σ_K) measurements.

Table 1 summarizes the structural·properties of the TiCuH$_x$ and Ti$_2$CuH$_x$ samples as deduced from x-ray diffraction, neutron scattering, and proton lineshape parameters. The preparation procedures have been previously described.[1-5]

Table 1. Descriptions of TiCuH$_x$ and Ti$_2$CuH$_x$ and Hydrogen Diffusion Activation Energies (E$_a$)

Sample	Metal Sublattice Structure	Probable Hydrogen Site Occupancies	E$_a$ (eV)	Temperature Range (K)
$TiCuH_{0.94}$	Tetragonal	94% Ti$_4$ only	0.84±0.02	465 - 560
a-TiCuH$_{1.4}$	Amorphous	Mixed (mostly Ti$_4$ with some	0.45±0.02	357 - 410
		Ti$_{4-y}$Cu$_y$ and octahedral)	0.185±0.01	208 - 357
			0.09±0.01	150 - 207
$Ti_2CuH_{1.9}$	Orthorhombic (?)	∿95% Ti$_4$ (some Ti$_2$Cu$_4$ likely)	0.35±0.02	290 - 519
$Ti_2CuH_{2.63}$	Orthorhombic (?)	100% Ti$_4$ and 63% Ti$_2$Cu$_4$	0.29±0.02	290 - 395

Hydrogen diffusion behavior has been evaluated using the temperature dependence of the proton rotating-frame spin-lattice relaxation times[6] (T$_{1\rho}$) where the spin-locking field was about 7.3G and the proton resonance frequency was 34.5 MHz. The temperature dependences of the T$_{1\rho}$ data for Ti$_y$CuH$_x$ are shown in Fig. 1. Table 1 summarizes the diffusion activation energies (E$_a$) that have been deduced from the T$_{1\rho}$ data. Although a single E$_a$ corresponding to Arrhenius behavior represents proton mobility in the crystalline $TiCuH_{0.94}$ and Ti$_2$CuH$_x$, three E$_a$ values are required for amorphous a-TiCuH$_{1.4}$, which confirms the behavior previously seen[5] in a-TiCuH$_{1.3}$. Furthermore, E$_a$ is greatly reduced when protons occupy sites in addition to the tetrahedral Ti$_4$ interstitials. This effect is seen in both crystalline Ti$_2$CuH$_x$ and amorphous a-TiCuH$_{1.4}$. From a consideration of the TiCu and Ti$_2$Cu crystal structures,[1,4] hydrogen diffusion in crystalline TiCuH can only occur by nearest neighbor jumps between the Ti$_4$ sites,

while jumps through the intermediate Ti_2Cu_4 sites become possible in Ti_2CuH_x. This probably accounts for the lower E_a values for Ti_2CuH_x and similar (or even easier) jump-paths are available in the more disordered amorphous phase.

The magnetic susceptibilities (χ_m) for Ti_yCuH_x were measured between 80 K and 300 K and are summarized in Fig. 2. Although the χ_m values in Fig. 2 have been extrapolated to infinite magnetic field, the field-dependent ferromagnetic contribution was negligible except for a-$TiCuH_{1.4}$, which appears to have some magnetic impurities as well as an opposite temperature dependence for χ_m. There are several contributions[7] to χ_m, but only the paramagnetic term χ_p is directly related to $N(E_F)$, the density of electron states at the Fermi level E_F. Hence, caution should be exercised in correlating χ_m differences only to $N(E_F)$ changes. In particular, the larger χ_m for a-$TiCuH_{1.4}$ compared to $TiCuH_{0.94}$ probably reflects either ferromagnetic or orbital contributions[7] and not a greater $N(E_F)$ for the amorphous phase. However, the unusual[7,8] χ_m increase with hydrogen content for Ti_2CuH_x is believed to actually correspond to $N(E_F)$ becoming larger since the proton T_1 and σ_K parameters also indicate $N(E_F)$ increasing from $Ti_2CuH_{1.9}$ to $Ti_2CuH_{2.63}$.
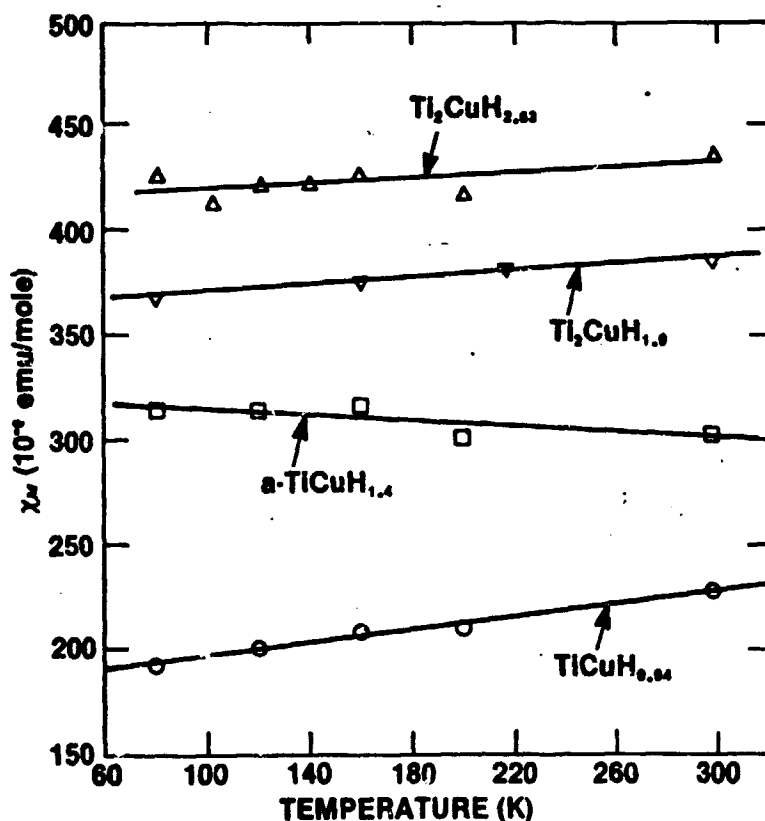

Fig. 2. Magnetic susceptibility values for $TiCuH_x$ and Ti_2CuH_x.

The proton T_1 and σ_K were measured at 56.4 MHz using methods previously described.[9] The σ_K values are referenced to tetramethylsilane. Table 2 summarizes the σ_K and $(T_{1e}T)^{-\frac{1}{2}}$ parameters, which are directly proportional[6,8,9] to $N(E_F)$, at the upper and lower temperature limits of the present NMR measurements. The negative σ_K values in Table 2 indicate that core-polarization[6] with d-electrons dominates proton hyperfine interactions in Ti_yCuH_x where the population of d-states is much larger than s-states as has been previously found in other Ti-based hydrides.[8,9] Futhermore, the proton parameters suggest $N(E_F)$ is significantly reduced in a-$TiCuH_{1.4}$ compared to crystalline $TiCuH_{0.94}$, while $N(E_F)$ increases with content in crystalline Ti_2CuH_x. However, a more detailed analysis based upon generalized Korringa relations[6] shows increased s-electron contact hyperfine interactions in the Ti_2CuH_x samples.

More extensive discussions of hydrogen diffusion and the electronic structures of Ti_yCuH_x will be published elsewhere.

Table 2. Proton Parameters $(T_{1e}T)^{-\frac{1}{2}}$ and Knight Shifts σ_K

Sample	T (K)	$(T_{1e}T)^{-\frac{1}{2}}$ $(sK)^{-\frac{1}{2}}$	σ_K (ppm)
$TiCuH_{0.94}$	300	0.163	-120
	80	0.150	-107
a-$TiCuH_{1.4}$	210	0.113	- 77
	80	0.108	- 87
$Ti_2CuH_{1.9}$	300	0.118	- 67
	115	0.115	- 69
$Ti_2CuH_{2.63}$	300	0.140	- 85
	80	0.145	- 91

ACKNOWLEDGEMENTS

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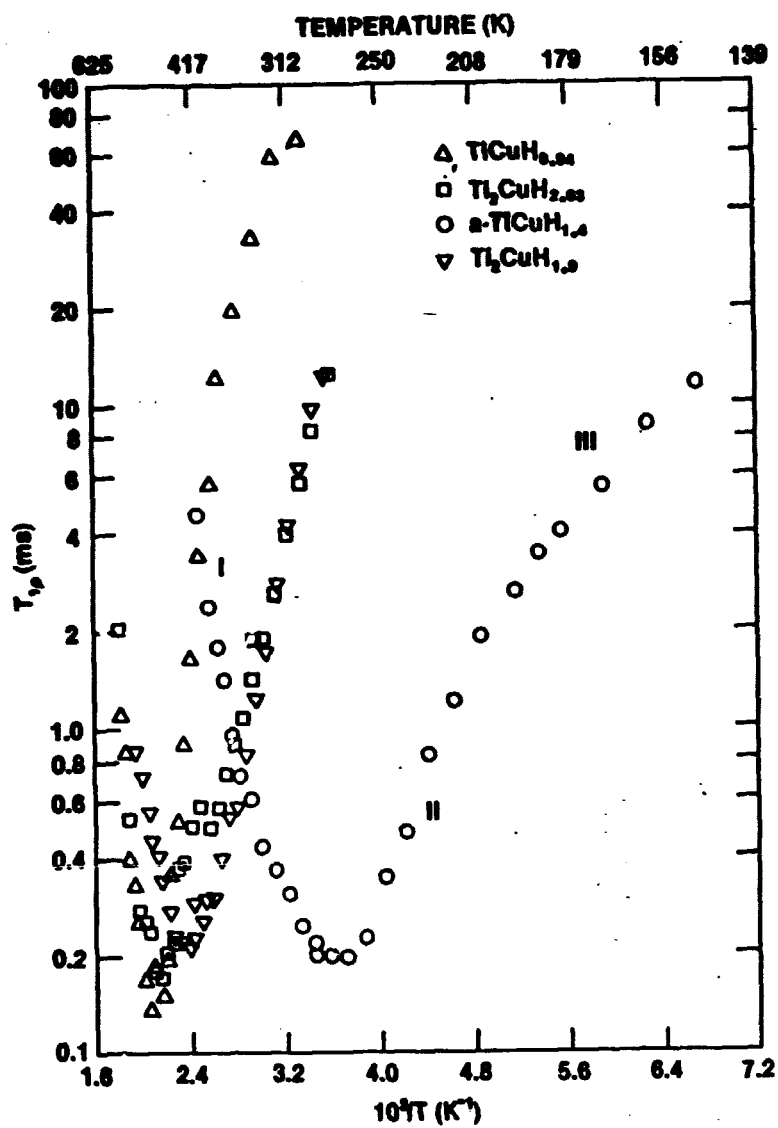
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Fig. 1.   Proton $T_{1\rho}$ relaxation times with $H_1 = 7.3$ G at $\nu_H = 34.5$ MHz.